



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B65D 23/08, C08G 59/18		A1	(11) International Publication Number: WO 99/12820 (43) International Publication Date: 18 March 1999 (18.03.99)
(21) International Application Number: PCT/US98/16839			(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 12 August 1998 (12.08.98)			
(30) Priority Data: 08/926,963 10 September 1997 (10.09.97) US			
(71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US).			
(72) Inventor: NIEDERST, Ken, W.; 4735 Lucy Drive, Allison Park, PA 15101 (US).			
(74) Agents: CHIRGOTT, Paul, S.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.			
			Published <i>With international search report.</i>

(54) Title: PLASTIC PACKAGE CONTAINERS HAVING IMPROVED GAS BARRIER PROPERTIES

(57) Abstract

The invention provides a plastic packaging container designed to store items that are carbonated and/or oxygen-sensitive and includes: (a) a plastic body having an opening through which an oxygen-sensitive and/or carbonated item can pass, (b) a closure which seals the container's opening, and (c) a label which covers at least 30 % of the plastic package body's exterior surface, wherein the closure and/or the label have enhanced gas barrier properties. The gas barrier label includes: (a) a layer of a thermoplastic, gas-permeable label material, and (b) a layer of a thermosetting gas barrier material. When a gas barrier label is used, its gas barrier layer is in intimate contact with the container's exterior surface. The gas barrier closure includes: (a) a thermoplastic, gas-permeable closure body, and (b) a layer of a thermosetting gas barrier material. The thermosetting gas barrier material used in making the label's and/or closure's gas barrier layer includes the reaction product of a polyamine (A) and polyepoxide (B), wherein polyamine (A) includes at least: (a) an initial polyamine; (b) an ungelled amine-epoxide adduct having active amine hydrogens which is the reaction product of the initial polyamine and at least: (i) epichlorohydrin, and (ii) a polyepoxide having a plurality of glycidyl groups linked to an aromatic member; or (c) initial polyamine reacted with formaldehyde and a phenol R⁵-OH where R⁵ is an aromatic group or fused aromatic group which may contain alkyl substitutions of 1-4 carbon atoms.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Republic of Korea	RO	Romania		
CU	Cuba	LC	Kazakhstan	RU	Russian Federation		
CZ	Czech Republic	LI	Saint Lucia	SD	Sudan		
DE	Germany	LK	Liechtenstein	SE	Sweden		
DK	Denmark	LR	Sri Lanka	SG	Singapore		
EE	Estonia		Liberia				

- 1 -

PLASTIC PACKAGE CONTAINERS HAVING IMPROVED GAS BARRIER PROPERTIES

5

BACKGROUND OF THE INVENTION

The technical field of the present invention relates to plastic containers designed to hold items which are oxygen-sensitive and/or carbonated, particularly to plastic food and beverage containers, and more particularly to plastic food and beverage containers 10 having labels and/or plastic closures which are coated with a gas barrier coating composition.

Plastic containers have found increasing use as replacements for glass and metal containers in today's packaging industry. Some advantages of plastic packaging over its glass counterpart include lighter weight, decreased breakage and potentially lower costs. On the other hand, one particular advantage of plastic packaging over its metal counterpart 15 (e.g., aluminum beverage cans) is that the former can more easily be designed as re-closable. However, notwithstanding the above, shortcomings in the gas barrier properties of common plastic packaging materials (e.g., polyesters, polyolefins and polycarbonates) present major problems to those in the packaging industry, and especially when such materials are used to package oxygen-sensitive items and/or carbonated beverages.

20 Specifically, gases such as oxygen and carbon dioxide can readily permeate through most of the plastic materials commonly used by the packaging industry. The oxygen permeability constant (herein referred to as "OPC") of such plastic materials quantifies for the packaging industry the amount of oxygen which can pass through a film or coating under a specific set of circumstances and is generally expressed in units of cubic centimeters-mil/100 square inches/atmosphere/day. This is a standard unit of permeation measured as 25 cubic centimeters of oxygen permeating through 1 mil (25.4 micron) thickness of a sample, 100 square inches (645 square centimeters) in area, over a 24-hour period, under a partial pressure differential of one atmosphere at specific temperature and relative humidity (R.H.) conditions.

30 Similarly, the carbon dioxide permeability constant (herein referred to as "CPC") of such plastic materials quantifies for the packaging industry the amount of carbon dioxide which can pass through a film or coating under a specific set of circumstances and is

- 2 -

also generally expressed in units of cubic centimeters-mil/100 square inches /atmosphere/day. This is a standard unit of permeation measured as cubic centimeters of carbon dioxide permeating through 1 mil thickness of a sample, 100 square inches in area, over a 24-hour period, under a partial pressure differential of one atmosphere at specific 5 temperature and relative humidity conditions. As used herein, OPC and CPC values are reported at 30° C. and 50% R.H. unless otherwise stated.

When compared to oxygen, carbon dioxide can more readily pass through the walls of a plastic container. Accordingly, if a plastic container has a relatively low CPC, it would have an even lower OPC. In the packaging industry, OPCs greater than 5.0 are often 10 considered unacceptably high when the container is designed to store an oxygen and/or carbonated item. On the other hand, OPCs less than 2.0 are often considered acceptable for this purpose. However, in instances where the item being stored is highly sensitive to oxygen, the industry often requires that the package have an OPC of less than 1.0. and even sometimes less than 0.1. Since it is very difficult to economically achieve such low OPCs 15 with the use of plastic containers, the industry continues to use glass and metal containers for this purpose. Unless otherwise stated, the term "gas permeability constant" or "GPC" will be used herein to refer to an OPC and/or a CPC.

Many foods, beverages, chemicals, medicines, medical supplies and the like are sensitive to oxidation. Accordingly, it is desirable to store them in a container which 20 minimizes the ingress of oxygen through its surfaces. On the other hand, since carbonated beverages require the presence of a certain amount of carbon dioxide so as to avoid from being considered "flat," it is desirable to store them in a container which minimizes the egress of carbon dioxide through its surfaces. As used herein, the term "flat" refers to a carbonated beverage losing at least about 10% of its original carbonation level, typically at 25 least about 15% of its original carbonation level, and more typically at least about 20% of its original carbonation level. It is for the above reasons that, since oxygen and carbon dioxide readily pass through most plastic materials used by the packaging industry (e.g., poly(ethylene terephthalate)), the shelf-life of oxygen sensitive and/or carbonated items stored in conventional plastic containers is significantly less than that observed when the 30 same items are stored in glass or metal containers.

Some examples of oxygen sensitive items whose shelf-life would be greatly reduced if stored in conventional plastic containers are perishable foods and beverages such

- 3 -

as tomato-based products (e.g., ketchup, tomato sauces and tomato pastes), juices (e.g., fruit and vegetable juices) and carbonated alcoholic beverages (e.g., beer, ale, malt beverages, sparkling wines, champagnes, and the like). In these instances, exposure to minute amounts of oxygen over a relatively short period of time can cause spoilage of the product and/or 5 adversely affect their taste. Some examples of carbonated beverages whose shelf-life would be greatly reduced if stored in conventional plastic containers are soft drinks, malt beverages, sparkling water, sparkling wines, champagnes, and the like.

One of the most common plastic packing materials used today by the food and beverage industry is poly(ethylene terephthalate) ("PET"). Notwithstanding its 10 widespread use, PET has a relatively high OPC (i.e., about 6.0). As such, the food and beverage packaging industry has sought ways to improve the OPC of such packaging materials. It should be noted that, typically, carbon dioxide permeates through a film and/or coating more readily than does oxygen. For example, PET has a CPC of about 20.

One of the methods disclosed in the literature as a means of improving a 15 plastic packaging material's GPC pertains to chemically and/or physically modifying the plastic. This method is typically expensive and creates recyclability problems.

Another method disclosed in the literature as a means of improving a plastic packaging material's GPC pertains to coating the plastic material with a gas barrier material (e.g., a gas barrier coating composition or a gas-barrier film).

20 One example of a method which improves the OPC of a conventional plastic packaging material by the use of a gas barrier coating composition is disclosed in co-pending, U.S. Patent Application Serial No. 221,161 which was filed on March 31, 1994. Specifically, the invention disclosed in that Application is an improvement in polyepoxide-polyamine resin based liquid barrier coatings which are suitable for use on polymeric 25 containers and other packaging materials. According to U.S.S.N. 221,161, the coatings disclosed therein not only have exceptionally low oxygen and/or carbon dioxide permeabilities, but also have the ability to maintain these excellent barrier properties under high humidity conditions considerably better than other polyepoxide-polyamine based barrier coatings.

30 The polyamine employed in U.S.S.N. 221,161 is an adduct of a polyamine having high aromatic content reacted with epichlorohydrin, certain polyepoxides, novolac epoxy resin, bisphenol F epoxy resin, or with phenol and formaldehyde to form Mannich

- 4 -

base. That polyamine adduct is then cured with polyepoxide which also may have aromatic content, with the exclusion of bisphenol A epoxy resins.

U.S.S.N. 221,161 also pertains to a packaging material which includes at least one layer of a relatively gas-permeable polymeric material and at least one layer of a polyamine-polyepoxide barrier coating as defined above. According to that Application, the composite packaging material exhibits gas permeabilities as set forth above in connection with the description of the barrier coating itself. The barrier coating included in the packaging material may be applied to one or more surfaces of the polymeric material, or it may be laminated between two layers of the polymeric material.

U.S.S.N. 221,161 contemplates the use of stock sheets that may be used as wrappings or formed into containers or other articles. U.S.S.N. 221,161 also contemplates that, alternatively, a container or other article may be formed from the polymeric material and the barrier coating of that invention applied onto the surface of the formed article such as by spraying, roll coating, or other conventional method of coating.

On the other hand, one example of a method which improves the OPC of a conventional plastic packaging material by the use of a gas barrier film is disclosed in U.S. Patent No. 5,232,754. Specifically, that Patent discloses a multilayer barrier layer for PET beverage bottles consisting of a layer of a polyvinyl alcohol (PVOH) or a ethylene vinyl alcohol (EVOH) polymeric film positioned between outer protective layers of a

thermoplastic polymer. The outer thermoplastic layers are needed to protect the EVOH or PVOH film from exposure to moisture which will severely degrade the films' gas barrier properties. That Patent also discloses a non-preferred multilayer barrier label consisting of an outer layer of a protective thermoplastic film and an inner barrier layer of an EVOH or PVOH film which contains label information reverse printed on the barrier layer. According to that Patent, one major problem with the use of a multilayer label is that the printing inks have a tendency of interfering with the gas barrier properties of the EVOH or PVOH film. Another problem disclosed in that Patent which is associated with the use of a multilayer label is that an adhesive may be required to bond the gas barrier layer to the inner and outer protective layers of the multilayer label.

The use of a gas barrier coating composition and/or a gas barrier film is typically less expensive than modifying the plastic as set out above. However, while these methods also create fewer recycleability problems, some still remain. For example, one

- 5 -

major recycleability problem which remains is associated with the recyclers' desirability of having a relatively pure raw material stream. Accordingly, since the recyclers do not want contaminants such as gas barrier coating compositions and/or gas-barrier films present in the final product, these gas barriers, if present, need to be removed before and/or during the

5 recycling process. As can be expected, it is very difficult to remove a gas barrier film which is sandwiched between two layers of PET. Moreover, while it is much easier to remove some gas barrier coatings sprayed onto the outer surface of a PET bottle, the removal process typically requires the recycler to add additional process steps to their current procedure.

Yet another method disclosed in the literature as a means of improving a

10 plastic packaging container's GPC is the use of a gas barrier adhesive to affix a label thereto. One example of such an attempt is disclosed in U.S. Patent No. 4,601,926. That patent discloses adhering a gas barrier label made from an aluminum foil to a plastic bottle with a heat-activated thermoplastic co-polyester resin adhesive that also has gas barrier properties. While the method disclosed in that patent reportedly improves the resulting plastic packaging 15 container's GPC, it will likely result in many recycling problems since the gas barrier adhesive is designed to tenaciously adhere to the plastic bottle. Accordingly, the implementation of the gas barrier adhesive disclosed in that patent would ultimately hinder the removal of the barrier label prior to or during conventional recycling procedures.

Those in the packaging industry would greatly welcome a plastic packaging 20 container which not only provides excellent shelf-life of oxygen-sensitive and/or carbonated items stored therein, but also does so in an economical manner which does not adversely affect the recycleability of the package. To date, no such plastic packaging material exists.

SUMMARY OF THE INVENTION

25 One object of this invention is to provide a plastic packaging container which, while having significantly improved gas barrier properties, can easily be recycled by conventional practices.

This and other objects of the present invention are provided by a novel 30 plastic packaging container. The novel plastic packaging container comprises: (a) a plastic package body having an opening through which an oxygen-sensitive and/or carbonated item can be introduced into the container's hollow cavity, (b) a closure designed to seal the container after its contents have been placed therein, and (c) a label designed to cover at least

- 6 -

30% of the plastic package body's exterior surface. When practicing this invention, the particular label and/or closure employed provide enhanced gas barrier properties to the resulting plastic packaging container. Henceforth, the label providing enhanced gas barrier properties to the plastic packaging container is referred to as a "gas barrier label;" and the 5 closure providing enhanced gas barrier properties to the plastic packaging container is referred to as a "gas barrier closure." Gas barrier labels and gas barrier closures are to be differentiated from their conventional counterparts. While, for optimum gas barrier performance, it is preferred for the resulting plastic packaging material to include both, a gas barrier label and a gas barrier closure, when less than optimum performance is desired, the 10 gas barrier label and a gas barrier closure can be used independently from one another.

The gas barrier label used when practicing this invention is comprised of:

(a) a layer of a thermoplastic, gas-permeable label material; and (b) a layer of a thermosetting gas barrier material. The thermosetting gas barrier material layer is positioned such that, when the gas barrier label is covering a portion of the plastic package body's 15 exterior surface, the label's thermosetting gas barrier material layer is in intimate contact with the plastic package body's exterior surface.

The gas barrier closure used when practicing this invention is comprised of:

(a) a layer of a thermoplastic, gas-permeable closure material; and (b) a layer of a thermosetting gas barrier material. The thermosetting gas barrier material layer is positioned 20 such that, when the gas barrier closure is sealing the plastic package body's opening, the closure's thermosetting gas barrier material layer is at least on that portion of the closure's exterior surface which is directly aligned with the plastic package body's opening.

The gas barrier material of the present invention comprises the reaction product of a polyamine (A) and polyepoxide (B), wherein polyamine(A) comprises at least 25 one of the following:

- (a) an initial polyamine;
- (b) an ungelled amine-epoxide adduct having active amine hydrogens which is the reaction product of the initial polyamine and at least one of the 30 following:
 - (i) epichlorohydrin,

- 7 -

- (ii) a polyepoxide having a plurality of glycidyl groups linked to an aromatic member; or
- (c) initial polyamine reacted with formaldehyde and a phenol

R^5-OH

5 where R^5 is an aromatic group or fused aromatic group which may contain alkyl substitutions of 1-4 carbon atoms.

10 Due to the unique features of the plastic packaging containers encompassed by the present invention, they have significantly improved gas barrier properties and can easily be recycled by conventional practices.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevational view of a plastic bottle having a gas barrier label affixed to the side wall of the bottle and a gas barrier closure for sealing its opening.

15 FIG. 2 is a cross sectional view of the plastic bottle of FIG. 1 taken through line 2-2 so as to show the physical relationship between the layers of the gas barrier label and the exterior surface of the bottle.

20 FIG. 3 is a cross-sectional view of the gas barrier closure for the plastic bottle of FIG. 1 taken through line 3-3 so as to show the physical relationship between layers of the gas barrier closure.

DETAILED DESCRIPTION OF THE INVENTION

The plastic packaging container of this invention is especially useful for holding items which are oxygen-sensitive and/or carbonated. These packaging containers include: (a) a plastic package body having an opening through which the oxygen-sensitive and/or carbonated item can be introduced into the container, (b) a gas barrier closure designed to seal the container after its contents have been placed therein, and/or (c) a gas barrier label designed to cover at least a portion of the plastic package body's exterior surface. The particular gas barrier label and/or gas barrier closure employed provide enhanced gas barrier properties to the resulting plastic packaging container due to their improved gas barrier properties. While, for optimum gas barrier performance, it is preferred for the resulting plastic packaging material to include both, a gas barrier label and a gas

- 8 -

barrier closure, when less than optimum performance is desired, the gas barrier label and a gas barrier closure can be used independently from one another.

If a gas barrier label is used when practicing this invention either by itself or in conjunction with a gas barrier closure, in order to observe a noticeable improvement in the 5 gas barrier properties of the resulting plastic packaging container, the gas barrier label is typically designed to cover at least 30% of the plastic package body's exterior surface, more typically at least 40% of a plastic package body's exterior surface, and even more typically at least 50 % of a plastic package body's exterior surface. If less than 30% of the plastic package body is covered by the gas barrier label, there will not be a sufficient improvement 10 in gas barrier properties of the resulting plastic packaging container.

On the other hand, while it is within the scope of this invention to cover up to 100% of the plastic package body with the gas barrier label, a coverage of over 90% is typically not economically desirable. In most practices, the gas barrier label is typically designed to cover not more than 90% of the plastic package body, more typically not more 15 than 80%, and even more typically not more than 70%.

The preferred size and shape of the gas barrier label depends, in part, on parameters such as: the desired end use of the resulting plastic packaging container, the GPC of the plastic package body, the GPC of the gas barrier label, the GPC of the gas barrier closure (if employed), and the like. Notwithstanding the above, those skilled in the art can 20 readily determine the preferred size and shape of the gas barrier label after reading this specification.

As used herein, the term "gas barrier label" refers to a label which has a GPC of at least 10% less than that of the plastic package body over which it is applied. Typically, in order to observe a noticeable improvement in the gas barrier properties of the resulting 25 plastic packaging container, the gas barrier label's GPC is typically at least 20% less than that of the package body, and more typically at least 30% less than that of the package body.

The preferred GPC of the gas barrier label depends, in part, on parameters such as: its size and shape, the desired end use of the resulting plastic packaging container, the GPC of the plastic package body, the GPC of the gas barrier closure (if employed) and 30 the like. Notwithstanding the above, those skilled in the art can determine the preferred GPC of the gas barrier label after reading this specification.

- 9 -

On the other hand, if a gas barrier closure is used when practicing this invention either by itself or in conjunction with a gas barrier label, in order to observe a noticeable improvement in the gas barrier properties of the resulting plastic packaging container, the gas barrier closure is typically designed to completely seal the container's opening so as to minimize the amount of gas leakage between the closure's and package's interfacing surfaces.

5 The preferred size and shape of the gas barrier closure depends, in part, on parameters such as: the desired end use of the resulting plastic packaging container, the GPC of the plastic package body, the GPC of the gas barrier closure, the GPC of the gas barrier label (if employed), and the like. Notwithstanding the above, those skilled in the art can 10 readily determine the preferred size and shape of the gas barrier closure after reading this specification.

15 As used herein, the term "gas barrier closure" refers to a closure which has a GPC of at least 10% less than that of the closure's body over which it is applied. Typically, in order to observe a noticeable improvement in the gas barrier properties of the resulting plastic packaging container, the gas barrier closure's GPC is typically at least 20% less than that of the closure's body, and more typically at least 30% less than that of the closure's body.

20 The preferred GPC of the gas barrier closure depends, in part, on parameters such as: its size and shape, the desired end use of the resulting plastic packaging container, the GPC of the plastic package body, the GPC of the gas barrier label (if employed), and the like. Notwithstanding the above, those skilled in the art can determine the preferred GPC of 25 the gas barrier closure after reading this specification.

30 One example of a plastic packaging container encompassed by the present invention is illustrated in FIG. 1. Specifically, in FIG. 1, plastic packaging container 5 has gas barrier label 10 positioned over the side wall 12 of plastic package body 14. Plastic package body 14 has an opening 15 defined therein through which oxygen-sensitive and/or carbonated items can be introduced into the body's hollow cavity. Plastic packaging container 5 also has a closure 17 designed to seal the container after its contents have been placed therein.

The plastic package body can be made of any suitable polymeric material. The preferred material from which the plastic package body is made depends, in part, on

- 10 -

parameters such as: the desired contents of the plastic packaging container and the processing conditions, if any, of these contents after being placed into the plastic packaging container, the conditions under which the plastic packaging container will be manufactured, processed, filled, shipped, stored and/or recycled, the GPC of the gas barrier label, and the like.

Notwithstanding the above, when practicing the present invention, the plastic package body typically comprises at least one of the following: poly(methylmeth-acrylate), polycarbonate, polyvinyl chloride, polyvinyl acetate, poly(ethylene terephthalate), polystyrene, polyethylene, polypropylene, poly(ethylene naphthalate) and

polytetrafluoroethylene. The preferred material(s) from which the plastic package body is made depends, in part, on parameters such as: the desired end use of the resulting plastic packaging container, the GPC of the particular material from which the plastic package body is to be made, the GPC of the gas barrier label, and the like. Notwithstanding the above, those skilled in the art can readily determine the preferred material(s) from which to make the plastic package body after reading this specification. However, due to cost and availability, the plastic packaging industry presently prefers to use at least one of the following materials when making the plastic package body: polyvinyl chloride, polyvinyl acetate, poly(ethylene terephthalate), polystyrene, polyethylene, poly(ethylene naphthalate), polypropylene and polytetrafluoroethylene.

The gas barrier label of this invention comprises: (a) a thermoplastic, gas-permeable label material layer, and (b) a thermosetting gas barrier material layer. The thermoplastic, gas-permeable material layer is typically treated to facilitate adhesion of the gas barrier material layer thereto. The types of treatment procedures which can be used when practicing this invention will be described later in this specification.

The thermoplastic, gas-permeable label material layer can be made from any suitable material. The preferred material from which the thermoplastic, gas-permeable label material layer is made depends, in part, on parameters such as: the desired end use of the resulting plastic packaging container, the GPC of the plastic package body, the GPC of the thermosetting gas barrier label layer, the GPC of the thermoplastic, gas-permeable label material layer, and the like.

If the resulting plastic packaging container is designed to store carbonated beverages, the thermoplastic, gas-permeable label material layer will typically comprise: a

- 11 -

polyolefin (e.g., polypropylene and/or polyethylene), a polyamide, a polyester, paper and mixtures thereof. According to present industry standards, the most widely used thermoplastic, gas-permeable label material for plastic carbonated beverage containers are comprised of polyolefins, and particularly, of a two-layer lamination of polypropylene films, 5 with the outside layer being a transparent polypropylene layer of about 0.5 mils (13 microns) thick. Typically this transparent layer is reverse printed with label graphics on the inside surface, and the inside layer is an opaque polypropylene layer of about 1 mil (25 microns) thick which is used to accentuate the printed label graphics. For purposes of this application, a label material made from a two layer lamination of polyolefin films is considered one layer 10 of thermoplastic, gas-permeable label material. Other embodiments of this invention may include a thermoplastic, gas-permeable label material made from only one layer with the graphics being reverse printed on its inside surface such that the graphics are between the thermoplastic, gas-permeable label material and the gas-barrier coating material. It is also within the scope of this invention to reverse print graphics on the gas-barrier material layer's 15 inside surface such that the graphics are between the gas barrier material layer and the plastic package body.

However, notwithstanding the above, those skilled in the art can readily determine the preferred material from which the thermoplastic, gas-permeable label material layer is made after reading this specification.

20 As stated above, the thermoplastic gas-permeable label material is typically pretreated to oxidize the label material surface before application of the thermosetting gas barrier material. This is done in order to facilitate adhesion of the thermosetting gas barrier material thereon. The oxidative pretreatment increases the surface tension of the thermoplastic gas-permeable label material surface, thereby enhancing the adhesion of the 25 gas barrier material and/or printing inks thereto. Several treatment methods can be employed to oxidize the surface of the thermoplastic gas-permeable label material. These include: flame treatment, plasma treatment and corona treatment. The presently preferred method of oxidizing the surface of the thermoplastic gas-permeable label material is by a corona treatment.

30 A corona treatment typically requires an equipment arrangement which consists of a high frequency generator, high voltage transformer and a treater station assembly that includes a dielectric covered grounded roll and an electrode. In principle, the

- 12 -

air gap between the electrode and the moving label material surface has a lower dielectric breakdown voltage than the label material substrate. As high frequency, high voltage power is applied across the electrode, air gap, label material substrate and the grounded roll assembly, the air in the gap becomes ionized and forms a gaseous conductor that can be seen 5 as a bluish corona. Accelerating electrons in the ionized air gap gain energy as they move away from the negative electrode towards the positive grounded roll. These accelerating electrons simultaneously collide with other gas molecules to create oxidative molecules such as ozone and oxygen free-radicals. Electrons impact the label material surface with energies two or three times that required to break molecular bonds on the substrate surface. Resulting 10 free-radicals on the label materials substrate surface react rapidly with oxidizing products developed in the corona. Oxidation of solid surfaces increases surface energy, thus allowing better wetting by liquids and promoting adhesion.

The general and preferred thermosetting gas barrier coating materials used when practicing this invention will be described later in this specification. However, with 15 regard to their physical orientation, the thermosetting gas barrier material layer is positioned on the gas barrier label such that, when the label covers a portion of the plastic package body's exterior surface, the label's thermosetting gas barrier material layer is in intimate contact with a portion of the plastic package body's exterior surface. The physical 20 relationship between the gas barrier label's thermoplastic, gas-permeable and gas barrier layers and the plastic package body's exterior surface is illustrated in FIG. 2 which is the cross-sectional view of the plastic packaging container of FIG. 1 taken through line 2-2.

As shown in FIG. 2, when gas barrier label 10 is positioned onto plastic package body 14, the exterior surface 12 of plastic package body 14 is in intimate contact with the gas barrier layer 22 of label 10. It should be noted that the dimensional thicknesses 25 of the various layers illustrated in FIG. 2 are significantly enlarged to show detail. Moreover, these dimensional thicknesses are not proportional. The intent of FIG. 2 is merely to show the physical relationship of the plastic packaging container's various layers.

FIG. 2 also shows an optional embodiment of the present invention wherein a second gas barrier layer 24 is positioned over on the exterior surface 26 of thermoplastic, 30 gas-permeable layer 20. If present, this second gas barrier layer can be comprised of a thermoplastic or thermosetting gas barrier material. Specific examples of thermoplastic and

thermosetting gas barrier materials which can be used when practicing this invention will be discussed later in this specification.

The gas barrier material used to form the gas barrier material layer of the present invention has unique adhesion properties. Specifically, the gas barrier material used when practicing this invention adheres well to the polymeric gas permeable layer of the label and/or closure, even to the extent that the two layers typically do not separate from one another during conventional plastic recycling processes (e.g., those conventionally used to recycle plastic beverage bottles). Accordingly, the use of adhesives, tie layers or the like between the polymeric gas permeable layer and the thermosetting gas barrier material are typically not necessary. On the other hand, the gas barrier material used when practicing this invention does not adhere well to the plastic package body of the plastic packaging container. Accordingly, during conventional plastic recycling processes, the gas barrier layer is easily separated from the plastic package body with little, if any, trace of the thermosetting gas barrier material layer being present on the plastic package body's exterior surface. As explained above, this is a highly desirable feature to those in the plastic packaging and recycling industries.

The gas barrier labels of this invention can be applied onto the plastic package body by any suitable means. In order to facilitate recyclability of the final plastic packaging container, it is presently preferred to affix the gas barrier label onto the plastic package body by using as little adhesive as possible. One technique which minimizes the amount of adhesive employed is the standard industry practice of placing labels on plastic carbonated beverage bottles. This particular technique comprises the steps of: (a) spot or strip tacking one end of the label to the plastic package body with an adhesive, (b) wrapping the label completely around the container, and (c) glue sealing the label overlap onto the exterior surface of the label.

When filled, most plastic containers experience at least some slight expansion. This is especially true when the contents stored therein are carbonated beverages. In most instances, the expansion of the container during filling and/or storing is desirable since it tightens the seal between the plastic package body and the gas barrier label, thus even further improving the container's barrier properties.

When practicing this invention, it is not necessary for the gas barrier label to completely encircle the plastic package body. For those embodiments wherein the gas

- 14 -

barrier label does not completely encircle the plastic package body, it is preferred to minimize the amount of adhesive used to affix the label onto the body. One example of such a technique comprises the utilization of a bead of adhesive around the entire inner periphery of the gas barrier label. Using adhesive on essentially the entire inner surface of the gas

5 barrier label to attach the label to the plastic package body is outside the scope of this invention since it would significantly impair the recyclability of the resulting plastic packaging container when conventional recycling practices are employed..

The plastic packaging containers of this invention further comprise a closure which is designed to seal the opening defined in the plastic package body. These closures 10 can be designed to be unusable after the container is opened for the first time (e.g., pull-top or pop-top closures), or reusable (e.g., screw-top closures). Any suitable type of closure can be used when practicing this invention. Moreover, the closures used when practicing this invention can be made of any suitable material.. Examples of such suitable materials include: plastics (e.g., polyolefins), metal and/or metal alloys (e.g., aluminum and steel), and the like. 15 The preferred closure will depend, in part, on parameters such as: the desired contents of the plastic packaging container and the processing conditions, if any, of these contents after being placed into the plastic packaging container, the conditions under which the plastic packaging container will be manufactured, processed, filled, shipped, stored and/or recycled, the GPC of the closure, and the like. Notwithstanding the above, those skilled in the art can 20 readily determine the preferred closure after reading this specification.

In those instances where the resulting plastic packaging container is designed for storing carbonated beverages, the type of closure typically employed by the industry is a screw cap made out of a polyolefin such as polypropylene and polyethylene. Since gases such as oxygen and carbon dioxide can readily permeate through polyolefins, in an optional 25 embodiment of this invention, a gas barrier closure is employed which comprises: (a) a thermoplastic, gas-permeable closure body, and (b) at least one gas barrier material layer. The physical relationship between the plastic closure body and gas barrier layer of a gas barrier closure is illustrated in FIG. 3 which is the cross-sectional view of the closure 17 of FIG. 1 taken through line 3-3.

30 As shown in FIG. 3, closure 17 includes plastic closure body 30 and gas barrier material layer 32. Gas barrier layer 32 is positioned on the outer top surface 34 of closure body 30. It is within the scope of this invention for the entire outer surface of closure

- 15 -

body 30 to be covered with a gas barrier layer. However, since in order for the gases to escape from the container through the side walls 36 of closure 17, they must first pass through the side walls of plastic package body which is sealed thereby, it is typically not economically feasible and/or necessary to apply a gas barrier layer to closure side walls 36.

5 When present on the thermoplastic, gas-permeable label layer or, optionally, on the multi-layer closure, gas barrier material layer can have any suitable dry film thickness. Although thicker coatings typically provide greater gas barrier protection, the packaging industry typically prefers thinner coating for appearance and/or economic reasons. As such, the gas barrier material layers of the present invention generally have a dry film thickness of
10 not more than about 1.0 mil (25.4 microns). If even thinner films are desired, the gas barrier material layers can often provide acceptable gas barrier properties at a dry film thickness of not more than about 0.5 mil (12.7 microns), and even of not more than about 0.3 mil (7.6 microns).

15 The gas barrier coating may be applied onto the thermoplastic, gas-permeable label layer or, optionally, on the closure as a single layer or as multiple layers. When multiple gas barrier material layers are employed, it is typically preferred to drive-off any solvent that might be present in a lower layer, prior to applying the next layer there over.

20 In one particular embodiment of the present invention, a sheet or film stock of the a thermoplastic, gas-permeable label material is coated with the gas barrier material to form a continuous sheet of a gas barrier label. This continuous sheet can then be cut to size to form individual gas barrier labels for use on individual plastic package bodies.

25 The thermosetting gas barrier coating material used when practicing this invention to form the gas barrier material layer for the gas barrier label or, optionally, for a gas barrier closure comprises the reaction product of a polyamine (A) and a polyepoxide (B). Polyamine (A) can be an initial polyamine, an ungelled polyamine adduct, or a mixture thereof. As used herein, the term "ungelled polyamine adduct" refers to an amine-functional polymeric resin which is a soluble and/or dispersible in a liquid medium.

30 The initial polyamine used as, or in the making of, polyamine (A) is typically characterized as having a substantial aromatic content. Specifically, at least about 50 percent of the carbon atoms in the initial polyamine are in aromatic rings (e.g., phenylene groups and/or naphthylene groups). Preferably the number of the initial polyamine carbon atoms in aromatic rings is at least about 60 percent, more preferably at least about 70 percent, and

- 16 -

even more preferably at least about 80 percent. This initial polyamine can be represented by the structure:



5

where:

k is 1.5 or greater,

Φ is an aromatic-containing organic compound, and

R^1 is an alkyl group having between 1 and 4 carbon atoms.

10 Preferably, k is 1.7 or greater, more preferably 1.9 or greater, and even more preferably, 2.0 or greater. Preferably, R^1 is not larger than C_3 , more preferably not larger than C_2 , and even more preferably not larger than C_1 . Preferably, Φ comprises an aryl group, and more preferably a benzyl or a naphthyl group.

15 The gas barrier coating compositions of the present invention can be produced without having to form an ungelled polyamine adduct. In instances where a polyamine adduct is not formed, all of the epoxide required for curing the gas barrier coating composition (*i.e.*, polyepoxide (**B**)) is blended with the initial polyamine (*i.e.*, polyamine (**A**)).

20 When an initial polyamine is pre-reacted to form an adduct, sufficient active amine hydrogen groups must be left unreacted so as to provide reaction sites for reacting during the final curing step. Typically, about 10 to about 80 percent of the active amine hydrogens of the polyamine are reacted with epoxy groups. Pre-reacting fewer of the active amine hydrogens reduces the effectiveness of the pre-reaction step and provides little of the linearity in the polymer product that is one of the advantages of forming the adduct.

25 In accordance with one embodiment, a polyamine adduct is formed by reacting the initial polyamine with epichlorohydrin. By carrying out the reaction at polyamine to epichlorohydrin molar ratios greater than about 1:1 in the presence of an alkali, a primary reaction product is polyamine groups joined by 2-hydroxypropylene linkages. The reaction of *m*-xylylenediamine ("MXDA"), a preferred polyamine, with epichlorohydrin is 30 described in U.S. Patent No. 4,605,765, and such products are commercially available under the tradenames GASKAMINE 328® and GASKAMINE® 328S from Mitsubishi Gas Chemical Company.

- 17 -

In accordance with another embodiment, a polyamine adduct is formed by reacting the initial polyamine with polyepoxides in which a plurality of glycidyl groups are linked to an aromatic member. As used herein, the term "linked" refers to the presence of an intermediate linking group. Such polyepoxides can be represented by Formula (I):

5



where:

10 R^2 is phenylene or naphthylene;

X is the intermediate linking group and is N, NR^3 , CH_2N , CH_2NR^3 , O, and/or $\text{C}(\text{O})-\text{O}$, where R^3 is an alkyl group containing 1 to 4 carbon atoms, a cyanoethyl group or cyanopropyl group;

n is 1 or 2; and

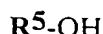
15 m is 2 to 4.

Examples of such polyepoxides include: N,N,N',N'-tetrakis (oxiranylmethyl)-1,3-benzene dimethanamine (e.g., that which is commercially available under the tradename TETRAD X epoxy resin from Mitsubishi Gas Chemical Co.), resorcinol diglycidyl ether (e.g., that which 20 is commercially available under the tradename HELOXY® 69 epoxy resin from Shell Chemical Co.), diglycidyl esters of phthalic acid (e.g., that which is commercially available under the tradename EPI-REZ® A-100 epoxy resin from Shell Chemical Co.), and triglycidyl para-aminophenol (e.g., that which is commercially available under the tradename Epoxy Resin 0500 from Ciba-Geigy Corporation).

25 In another embodiment, a polyamine adduct is formed by the reaction of the initial polyamine with a novolac epoxy resin or a bisphenol F epoxy resin. Notably excluded are bisphenol A type epoxy resins. Preferred in this group are diglycidyl novolacs such as that which is commercially available under the tradename DEN-431 from Dow Chemical Co. Alternatives include novolacs with higher glycidyl functionality such as those which are 30 commercially available under the tradenames DEN-438 and DEN-439, also from Dow Chemical Co.

- 18 -

In still another embodiment, forming the polyamine adduct involves formation of Mannich bases from reaction of the initial polyamine with formaldehyde and phenol of the structure



5

where:

R^5 is an aromatic group or fused aromatic group which may contain 1 to 4 carbon alkyl substitutions

A commercially available example in which the polyamine is metaxylylenediamine is
10 commercially available under the tradename ANCAMINE 1856 from Pacific Anchor
Chemical Corporation, a division of Air Products and Chemicals, Inc.

Notably excluded from the types of epoxides that can be reacted with the initial polyamine to form a polyamine adduct are bisphenol A type epoxy resins.

Alternatives for such bisphenol A type epoxides which can be reacted with the initial
15 polyamine in accordance with the present invention include novolacs with higher glycidyl
functionality (e.g., those which are commercially available from Dow Chemical Co. under
the tradenames DEN-438 and/or DEN-439).

The reaction of the epoxide and the initial polyamine to produce the ungelled adduct is carried out at temperatures and concentrations of reactants sufficient to produce the
20 desired ungelled product. These temperatures and concentrations will vary depending upon the selection of starting materials. Typically, however, reaction temperatures will range from about 40° C. to about 140° C., with lower temperatures (e.g., from about 40° C. to about 110° C.) being preferred for those systems that are more susceptible to gellation. Similarly, concentrations of reactants will typically range from about 5 to about 100 percent by weight
25 of reactant in an appropriate solvent depending upon the particular molar ratio and type of reactants. Lower concentrations of reactants are generally preferred for those systems that are more susceptible to gellation.

Specific reaction conditions can readily be chosen by one skilled in the art, guided by the disclosure and the examples herein. Moreover, preparation of an ungelled
30 polyamine adduct is also described in commonly-owned U.S. Patent No. 5,006,381, columns 2 through 7. The description in U.S. Patent No. 5,006,381, of the preparation of such polyamine adducts, is incorporated herein by reference.

- 19 -

In most instances, when compared to the non-adduct producing approach, forming the polyamine adduct typically has the advantage of increasing molecular weight while maintaining linearity of the resin, thereby avoiding gellation. This can be achieved, for example, by using an initial polyamine having no more than two primary amino groups.

5 Typically, the initial polyamines employed when practicing this invention react relatively slowly with polyepoxide (B). On the other hand, the aforementioned polyamine adduct reacts relatively quickly with polyepoxide (B). Accordingly, another advantage of forming the polyamine adduct is that the reaction period necessary to form the resulting gas barrier coating can be significantly reduced.

10 Polyepoxide (B) used when practicing this invention may be any epoxide known to those of skill in the art which can react with polyamine (A) to form gas barrier coating compositions. Preferably, polyepoxide (B) includes those polyepoxides in which a plurality of glycidyl groups are linked to an aromatic member. General examples of such polyepoxides include those represented by Formula (I) described earlier. Specific and 15 preferred examples of such a group of polyepoxides also include those described earlier which can be reacted with the initial polyamine to form the ungelled polyamine adduct.

20 When polyepoxides are employed in the formation of a polyamine adduct, they may be the same or different as those used as polyepoxide (B). Typically, if a polyamine adduct is used in the formation of the gas barrier coatings of this invention, the epoxides used in forming the polyamine adduct and those used as polyepoxide (B) have epoxy functionality of at least about 1.4, and preferably at least about 2.0. The presence of small amounts of monoepoxides may not, however, be objectionable.

25 Polyepoxide (B) may include polyepoxides that are saturated or unsaturated, aliphatic, cycloaliphatic, aromatic, or heterocyclic, and may be substituted with non-interfering substituents such as hydroxyl groups or the like. Generally, such polyepoxides may include polyglycidyl ethers of aromatic polyols, which may be formed by etherification of aromatic polyols with epichlorohydrin or dichlorohydrin in the presence of an alkali. Specific examples of such include: bis(2-hydroxynaphthyl)methane, 4,4'-dihydroxylbenzophenone, 1,5-dihydroxy-naphthalene and the like. Also included in the category of a suitable 30 polyepoxide (B) are polyglycidyl ethers of polyhydric aliphatic alcohols including cyclic and polycyclic alcohols.

- 20 -

The epoxy group equivalent weight of polyepoxide (B) is preferably minimized so as to avoid unnecessarily introducing molecular groups into the cured polymeric network that are not the preferred groups of this invention. Generally, polyepoxide (B) has a molecular weight above about 80. Preferably, the molecular weight of 5 polyepoxide (B) is in the range from about 100 to about 1,000, and more preferably from about 200 to about 800. Moreover, polyepoxide (B) generally has an epoxy equivalent weight above about 40. Preferably, the equivalent weight of polyepoxide (B) is in the range from about 60 to about 400, and more preferably from about 80 to about 300.

The diglycidyl ethers of an aromatic polyol such as bisphenol A or an 10 aliphatic alcohol such as 1,4-butanediol are not preferred when practicing the present invention. However, they may be tolerated when used to cure preferred embodiments of the polyamine adduct. Diglycidyl ethers of bisphenol F are preferred over bisphenol A based epoxides for the sake of low oxygen permeability. It is theorized that the presence of methyl groups in bisphenol A has a detrimental effect on gas barrier properties. Thus, 15 isopropylidene groups are preferably avoided. Other unsubstituted alkyl groups are believed to have a similar effect, and constituents containing such groups are preferably avoided in the present invention.

The polymers that comprise the chief film-forming resin of the gas barrier coating of the present invention are cured in situ when polyamine (A) and polyepoxide (B) 20 are mixed together. Each amine hydrogen of polyamine (A) is theoretically able to react with one epoxy group and is considered as one amine equivalent. Thus, a primary amine nitrogen is considered as difunctional in the reaction with epoxides to form the gas barrier coating.

For the purposes of this invention, these two components are typically 25 reacted in a ratio of the equivalents of active amine hydrogens in polyamine (A) to equivalent of epoxy group in polyepoxide (B) of at least about 1:1.5. In order to produce a gas barrier coating which is strong, flexible, moisture resistant and solvent resistant, the ratio of the equivalents of active amine hydrogens in polyamine (A) to equivalent of epoxy group in polyepoxide (B) is preferably in the range from about 1:1.5 to about 1:3.0, more preferably 30 from about 1:1.7 to about 1:2.8, and even more preferably from about 1:2.0 to about 1:2.5.

Preferably, the cured reaction product of polyamine (A) and polyepoxide (B) contains a substantial number of unreacted amine hydrogens. However, although

- 21 -

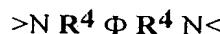
maximizing the amount of polyamine reactant is generally desirable for the sake of maximizing gas barrier properties, insufficient numbers of epoxy groups may not provide enough crosslinking to yield a film which is strong, moisture resistant and solvent resistant. On the other hand, the use of more epoxy than the preferred amounts may provide excessive 5 crosslinking to yield a film that is very brittle.

As the amount of amine nitrogen in the gas barrier coating increases, the coating's GPC values typically decrease. When practicing this invention, the amine nitrogen content in the cured gas barrier coating is typically at least about 6.0 weight percent. Preferably, the cured gas barrier coatings of this invention have an amine nitrogen content of 10 at least about 6.5 weight percent, and more preferably of at least about 7.0 weight percent. Typically, for economical reasons, the maximum amount of amine nitrogen content in the cured gas barrier coating of this invention is generally less than about 20 weight percent, more typically less than about 17 weight percent, and even more preferably less than about 15 weight percent. These weight percentages are based upon total resin solids weight of the 15 gas barrier coating.

Cured films of the gas barrier coating compositions prepared in accordance with the present invention have a molecular network that consists predominantly of two molecular groups:

(1) aminoalkyl substituted aromatic groups of the type

20



where:

25 \mathbf{R}^4 is an alkyl group containing not more than 4 carbons, preferably not more than 3, more preferably not more than 2, and even more preferably not more than 1 carbon atom), and

Φ is an aromatic-containing organic compound, and

(2) $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ (2-hydroxypropylene groups) groups.

30

Typically, the amount of the aminoalkyl substituted aromatic groups present in the cured gas barrier coating is at least about 50 weight percent, more preferably at least

- 22 -

about 55 weight percent, and even more preferably at least about 60 weight percent. The amount of the 2-hydroxy-propylene groups present in the cured gas barrier coating is typically at least about 20 weight percent, more preferably at least about 30 weight percent, and even more preferably at least about 40 weight percent. These weight percentages are

5 based upon the total weight of resin solids of the gas barrier coating. Examples of these embodiments include m-xylylenediamine adducted with epichlorohydrin or with N,N,N',N'-tetrakis (oxiranylmethyl)-1,3-benzene dimethanamine (TETRAD X epoxy resin) and cured with TETRAD X epoxy resin.

Excellent gas barrier properties can be attained when the cured film network 10 of the gas barrier coating contains at least about 70 weight percent of aminoalkyl substituted aromatic groups and/or 2-hydroxypropane groups. For the purposes of this invention, the gas barrier coating preferably contains at least about 80 weight percent of these two molecular groups, more preferably at least about 90 weight percent, and even more preferably at least about 95 weight percent. These weight percentages are based upon the total weight of resin 15 solids of the gas barrier coating.

As stated above, in one preferred embodiment, at least 50 percent of the carbon atoms in the initial polyamine used as, or in the making of, polyamine (A) are in an aromatic ring(s). In a particularly useful embodiment, R⁴ in the >N R⁴ Φ R⁴ N< group contains a single carbon atom. Accordingly, when Φ is a benzyl group, at least seventy 20 percent of the carbon atoms are in aromatic rings.

It should be understood, however, that the requisite amount of gas barrier properties necessary for the purposes of this invention may still be attained without the optimum levels of the aminoalkyl substituted aromatic groups and/or the 2-hydroxypropane groups molecular groups described above. For example, in addition to the aforementioned 25 preferred groups, some of the aminomethyl substitutions can be replaced with oxy substitutions, (i.e., -O-Φ-O- groups). These may be introduced into the network by adducting the initial polyamine with the polyglycidyl ethers of polyphenols (e.g., diglycidyl ether of resorcinol) or by curing one of the preferred adducts with such a polyglycidyl ether of a polyphenol. Additionally, some of the aminomethyl substitutions can also be replaced 30 with mixed substitutions such as -O-Φ-N< groups. These particular groups could be the residue of adducting or curing the initial polyamine with triglycidyl para-aminophenol.

- 23 -

Although not exhibiting performance properties which may be characterized as preferred for the purposes of this invention, the cured polymer network of the gas barrier coating can also include: -O-Φ-CH₂-Φ-O- groups, which are the residues of novolac epoxy resins or bisphenol F epoxy resins; and -O-C(O)-Φ-C(O)-O groups, which are derived from 5 diglycidyl esters of aromatic acids.

While maximizing the content of the aminoalkyl substituted aromatic groups and/or the 2-hydroxypropane groups present in the gas barrier coating is generally desirable, it has also been found to be additionally advantageous that the content of certain molecular groups be minimized in, or even essentially absent from, the gas barrier coating's cured 10 polymer network. For example, the groups that are preferably avoided include unsubstituted alkyl chains, particularly alkylene polyamine groups, as well as isopropylidene groups (*i.e.*, as in bisphenol A).

It should be apparent from the description herein that the desired molecular groups may be introduced into the cured polymeric network of the gas barrier coating by the 15 initial polyamine, the polyamine adduct or the epoxide curing component (*i.e.*, polyepoxide (**B**)). It should also be apparent that the various substitutions on the aromatic members described above may be provided in combination with each other on the same molecule in the reactants.

When practicing this invention, the gas barrier coating can be applied on to 20 the labels and/or the plastic closures as either a solvent-based or an aqueous-based thermosetting coating composition. If solvents are used, they should be chosen so as to be compatible with the thermoplastic, gas-permeable label material being coated, and also provide desirable flow properties to the liquid composition during application. Suitable solvents which can be used when practicing this invention include: oxygenated solvents, 25 such as glycol ethers (*e.g.*, 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-butoxyethanol, 1-methoxy-2-propanol and the like); or alcohols such as methanol, ethanol, propanol and the like. Glycol ethers, such as 2-butoxyethanol and 1-methoxy-2-propanol, are more preferred with 1-methoxy-2-propanol being most preferred. The use of 1-methoxy-2-propanol is preferred for its rapid evaporation rate, which minimizes solvent 30 retention in the cured film. In order to obtain desired flow characteristics in some of the embodiments using a pre-reacted adduct, use of 2-butoxyethanol may be preferred. Moreover, in embodiments not requiring slow evaporating solvents for the sake of flow

- 24 -

properties, the solvents listed here may be diluted with less costly solvents such as toluene or xylene. The solvent may also be a halogenated hydrocarbon. For example, a chlorinated hydrocarbon, such as methylene chloride, 1,1,1-trichloroethane and the like (usually considered fast evaporating solvents), may be especially useful in obtaining cured barrier

5 films. Mixtures of such solvents may also be employed. Non-halogenated solvents are preferred where the resultant barrier coating is desired to be halide-free.

The resin may also be in an aqueous medium (*i.e.*, the ungelled polyamine adduct may be an aqueous solution or dispersion). For example, when polyepoxide (B) is water-soluble (*e.g.*, the polyglycidyl ether of an aliphatic diol), the ungelled polyamine 10 adduct can be utilized as an aqueous solution. Otherwise, with water-insoluble polyepoxides, the ungelled polyamine adduct can have sufficient amine groups neutralized with an organic acid (*e.g.*, formic acid, lactic acid or acetic acid), or with an inorganic acid (*e.g.*, hydrochloric acid or phosphoric acid), to allow solubilization of the ungelled polyamine adduct in an aqueous medium. For such aqueous-based systems, an organic acid is typically preferred.

15 Generally, for embodiments employing the polyamine adduct approach, the solution of the polyamine adduct ready for application will have a weight percent of resin solids in the range of from about 15 weight percent to about 50 weight percent, and preferably from about 25 weight percent to about 40 weight percent. Higher weight percent solids may present application difficulties, particularly with spray application, while lower 20 weight percentages will typically require removal of greater amounts of solvent during the curing stage. For the embodiments which do not employ the polyamine adduct approach, solids contents above 50 weight percent can be applied successfully.

In a preferred embodiment, the gas barrier coatings of this invention further include a filler (C). It has been observed that the presence of a sufficient amount of a filler 25 having the appropriate particle size distribution even further improves the CPC and OPC values of the gas barrier coatings of this invention while maintaining a 20° gloss of at least 60% reflected light. In accordance with the embodiment of this invention which employs a filler to improve the coating's CPC and OPC value while maintaining a smooth and glossy appearance, filler (C) is typically characterized as a platelet-type filler which has the 30 following particle size distribution: (a) a number mean particle diameter ranging from about 5.5 to about 15 microns, and (b) a volume mean particle diameter ranging from about 8 to about 25 microns. Preferably, the platelet-type filler included in filler (C) has the following

- 25 -

particle size distribution: (a) a number mean particle diameter ranging from about 7.5 to about 14 microns, and (b) a volume mean particle diameter ranging from about 10 to about 23 microns; and more preferably the following particle size distribution: (a) a number mean particle diameter ranging from about 9.5 to about 13 microns, and (b) a volume mean particle diameter ranging from about 14 to about 20 microns. In addition to the above, in preferred embodiments of this invention, the platelet-type filler included in filler (C) further has the following particle size distribution: (a) at least about 55 percent by number of its particles having a diameter greater than 7 microns, and (b) less than about 15 percent by number of its particles having a diameter greater than 30 microns; preferably: (a) at least about 75 percent by number of its particles having a diameter greater than 7 microns, and (b) less than about 10 percent by number of its particles having a diameter greater than 30 microns; and more preferably: (a) at least about 95 percent by number of its particles having a diameter greater than 7 microns, and (b) less than about 5 percent by number of its particles having a diameter greater than 30 microns.

15 As used herein, the term "number mean particle diameter" refers to the sum of the equivalent circle diameter of all the particles in the sample that were analyzed divided by the total number of the particles that were analyzed.

As used herein, the term "equivalent circle diameter" refers to the diameter of a circle having a projected area equal to the projected area of the particle in the sample being analyzed.

As used herein, the term "volume mean particle diameter" refers to the cube root of the sum of the equivalent spherical diameter of all the particles in the sample that were analyzed divided by the total number of the particles that were analyzed.

As used herein, the term "equivalent spherical diameter" refers to the diameter of a sphere having a volume equal to the volume of the particle being analyzed.

All particle size measurements pertaining to the filler used when practicing the embodiment of this invention which employs filler (C) are as determined by a HORIBA LA-900 laser scattering particle size distribution analyzer from Horiba Instruments, Inc. in Irving, California. The HORIBA LA-900 works off the same principle as many conventional laser scattering particle size distribution analyzers.

For example, light traveling in a homogeneous medium travels in straight lines. However, when light travels through a medium containing particles of a material, the

- 26 -

particles cause the light to scatter. For a single particle, the amount of scattering in a particular direction depends upon the size, shape, and composition of the particle and the wavelength of the incident light. For a collection of particles, light scattered from all of the particles contributes to the total intensity of light scattered in a particular direction relative to 5 the incident light. By measuring the amount and/or intensity of light scattered throughout a number of angles relative to the incident light, it is possible to infer properties of the particles that induce the scattering. In particular, for particles of small size and similar composition, the pattern of scattered light is indicative of the sizes of the scattering particles.

Many conventional analyzers have used the aforementioned technique of 10 analyzing the scattered light intensity to determine the spectrum of particle sizes for a mixture of small particles of varying sizes. Particle size analyzers using this technique typically sample the angular distribution of the intensity of the light scattered from the mixture, process the data, and produce numerical values and possibly a graph or a histogram as output. The analyzer output represents the number or volume fraction of scattering 15 particles in the mixture as a function of the size of the particles and is usually called a particle size distribution.

For classical light scattering analysis, the problem of relating the angular distribution of scattered light to the size of the scattering particle has been solved 20 mathematically for the case of a spherical particle illuminated by a beam of unpolarized light. The mathematical solution is given by a theory proposed by Gustav Mie. The Mie theory is set forth in Chapter 4 of the book, *Absorption and Scattering of Light by Small Particles*, by Craig F. Bohren and Donald R. Huffman (John Wiley & Sons, 1983). Some particle size analyzers employ the Mie theory to determine particle size distributions from the observed pattern of scattered light.

25 Although such analyzers are not limited to the analysis of only samples containing particles of spherical shape, the particle sizes are reported as radii of spheres that are equivalent to the actual particles in terms of light scattering. For most applications, the equivalent-sphere specification of a particle size distribution is sufficient to characterize the actual particle size distribution. Mathematical models have also been derived for particular 30 particle shapes other than spherical, but they have been found to have limited value since, for scattering, only the average behavior of a large number of particles is of interest.

Since scattering is also a function of the wavelength of the incident light, some analyzers use incident light of a single wavelength. For this purpose, a laser has been the typical light source. Lasers have been used which produce light in the visible and near-visible wavelength range.

5 In many typical particle size distribution analyzers, a source of unpolarized light is projected in a beam to impinge upon a sample. The sample contains the particles whose sizes are under investigation. The particles are dispersed in the region of the sample that is illuminated by the incident light beam. The particles scatter light in patterns that are dependent on the ratio of the size of the particle to the wavelength of the light, and on the
10 refractive index of the particle material. The refractive index, a complex function of wavelength, is a measure of how much the light is refracted, reflected, and absorbed by the material. For a beam of unpolarized light incident on a random mixture of small particles, the scattering pattern is symmetric about the axis of the incident beam. The scattering is the result of the refraction, reflection, and absorption by the particles, as well as diffraction at
15 each particle surface where a light ray in the incident beam is tangent to the particle surface.

Light that scatters at a particular angle with respect to the incident beam may be rotated about the beam axis without changing the scattering angle. A large number of rays scattering from a single particle at a given scattering angle will fill all rotational orientations and thus form a cone of light, with the apex at the scattering particle and with the generating
20 angle (one-half the apex angle) of the cone equal to the scattering angle. The pattern of light rays scattering at all angles from a single particle may thus be thought of as made up of a continuous series of open cones of light, with the generating angle for a given cone corresponding to the scattering angle for the light comprising the surface of that cone. The axes of all of the cones are collinear with the line defined by the incident beam, and the
25 apexes of the cones are located at the scattering particle. At a distance from the scattering particle, a plane perpendicular to the incident beam will intersect a given cone in a circle. Planes not perpendicular to the incident beam will intersect a given cone in a curved line comprising a conic section (*i.e.*, an ellipse, a parabola, or a hyperbola), depending upon the orientation of the plane. Regardless of form, the curved line of intersection represents a
30 single scattering angle.

In particle size analyzers, it is not necessary to measure the scattering angle with infinite precision. Nevertheless, better angular resolution in the analyzer provides better

- 28 -

particle size resolution. In order to address angular precision effects directly, the set of all scattering angles falling between a precise lower angular limit and a precise upper angular limit will be referred to as an "angle class" of some intermediate angle. Light scattered within an angle class scatters into the region between two cones of slightly different size.

5 The smaller (inner) of the two cones is generated by the lower angular limit of the angle class and the larger (outer) cone is generated by the upper angular limit. The apexes of both cones are located at the scattering particle.

The inner and outer cones of an angle class define a circular annular region on a plane perpendicular to the incident beam and a more complex shaped region

10 (corresponding to a conic section) on a plane not perpendicular to the incident beam.

Scattered light rays intersecting the interior of such a region are rays which have scattered through an angle between the two generating angles of the cones. Thus any light ray intersecting such a region belongs to the angle class defined by that region. Some conventional analyzers employ ring-shaped light detectors to measure the amount of light

15 that scatters in an angle class determined by the radius and width of the ring and its distance from the scattering region. To correlate correctly the detected light with a scattering angle, these ring-shaped detectors are typically mounted and aligned precisely perpendicular to the incident beam.

Since the interaction region of the incident beam with the particles generally

20 has a finite extent, multiple particles at different locations in the incident beam will each contribute multiple overlapping cones of scattered light, with the apexes of the cones offset by the distance between the particles. Particles of the same size will have overlapping scattered-light cones of similar intensity variations, whereas particles of different sizes will have overlapping scattered-light cones of different intensity variations.

25 When the light beam illuminates a sample volume of finite extent, a converging lens may be used to direct parallel rays of light, each by definition scattered through the same scattering angle (by different particles), to a single point on a light detector in the focal plane of the lens. A lens that functions in this manner performs a Fourier transform, so that all light arriving at a given point on the detector is known to have been
30 scattered by the sample through a particular scattering angle, regardless of the location of the scattering particle in the sample volume.

- 29 -

The effect of the converging lens is to transform the spatial distribution of the scattered light it receives to that of an equivalent virtual system in which the light distribution in the focal plane of the lens is the same as if all the scattering particles were located at a point coincident with the optic center of the lens. The light detectors are placed 5 in the focal plane of the lens. The line from the optic center of the lens to the focal point of the lens is usually called the optic axis.

If a scattered ray passes through different refracting media, such as air and a sample suspension fluid, before detection, then an appropriate correction is typically applied to the ray's apparent angle of scatter to determine its true angle of scatter. Use of a lens and 10 recognition of the virtual scattering system simplifies the correction.

The intensity of light scattered as a function of scattering angle, when experimentally determined as above for a sample composed of many particles of a range of different sizes, consists of the summation of the scattered light from all the particles. If it is assumed that each size particle in the sample scatters light according to a given mathematical 15 theory and in proportion the relative number of such size particles present, then it is mathematically possible to determine from the experimental data the relative numbers of each size particle constituting the sample (*i.e.*, to determine the size distribution of the sample. The well-known mathematical process by which the size distribution may be extracted from the composite data is called an inversion process, or sometimes a deconvolution 20 process.

In the usual convention, a scattering angle of zero degrees coincides with unscattered light, and a scattering angle of 180 degrees represents light reflecting directly back into the incident beam. Scattering angles between 90 and 180 degrees are termed back scattering.

25 Similar to these conventional particle size distribution analyzers, the HORIBA LA-900 works by irradiating particles dispersed in a solution with a red light beam and a blue light beam which is obtained by filtering a tungsten lamp in parallel with an He-Ne laser. The particles cause the light to scatter at various angles. A condenser lens is used with an array detector at the focal point of the lens. There are also detectors positioned in the 30 front, side and rear of the sample. From the angular measurement of the scattered light by all the detectors, the particle size distribution of the sample is calculated. These computations are made by the particle size distribution analyzer by using the Mie scattering light theory.

- 30 -

Using the technique set out above, the HORIBA LA-900 laser scattering particle size distribution analyzer can provide an accurate, reproducible assessment of particle sizes in the range from 0.04 microns to 1,000 microns.

To measure particles having a diameter less than 0.1 microns, the HORIBA

5 LA-900 uses three separate detectors -- one for the front, side and rear scattering. As the light source for detecting scattering on the side and rear, the HORIBA LA-900 uses a tungsten lamp. In the HORIBA LA-900, the small angle forward scattered light is conventionally given by an He-Ne laser and detected by the ring detector and the large angle and rear scattered light is given by the tungsten lamp and detected by a photodiode. For a
10 complete description of how the HORIBA LA-900 works, see U.S. Patent No. 5,4278,443.

It has been observed that the incorporation of a sufficient amount of a platelet-type filler having a particle size distribution within the aforementioned particle size distribution parameters into a barrier coating comprising polyamine (A) and polyepoxide (B) as described herein can result in a gas barrier coating composition which, when cured, has an
15 OPC value of not more than 0.05 and a 20° gloss of at least 60% reflected light. However, it has also been observed that, when a platelet-type filler is used which has a particle size distribution outside of the aforementioned parameters, or if an insufficient amount of a platelet-type filler is used which has a particle size distribution within the aforementioned parameters, the resulting gas barrier coating may have an OPC value greater than 0.05 and/or
20 a 20° gloss less than 60% reflected light.

When filler (C) has the following particle size distribution: (a) a number mean particle diameter ranging from about 9.5 to about 15 microns, and (b) a volume mean particle diameter ranging from about 14 to about 25 microns, in order for the resulting gas barrier coating to have an OPC value of not more than 0.05 and a 20° gloss of at least 60%
25 reflected light, filler (C) is preferably present in an amount ranging from about 5 to about 50 weight percent, more preferably in an amount ranging from about 6 to about 45 weight percent, and even more preferably from about 7 to about 40 weight percent. These weight percentages are based upon the total solids weight of the gas barrier coating composition.

However, when the number mean particle diameter of filler (C) ranges from
30 about 5.5 to less than 9.5 microns, and/or when the volume mean particle diameter ranges from about 8 to less than 14 microns, in order for the resulting coating composition to have an OPC value of not more than 0.05, filler (C) is preferably present in an amount ranging

- 31 -

from about 12 to about 50 weight percent, more preferably in an amount ranging from about 15 to about 45 weight percent, and even more preferably from about 18 to about 40 weight percent. These weight percentages are based upon the total solids weight of the gas barrier coating composition.

5 Any suitable platelet-type filler which has the aforementioned particle size distribution and which is compatible with the barrier coating composition described above can be used when practicing this embodiment of the invention. Examples of such suitable fillers include: mica, vermiculite, clay, talc, micaeous iron oxide, silica, flaked metals, flaked graphite, flaked glass, flaked phthalocyanine, and the like. Of the fillers which have
10 the aforementioned particle size distribution parameters, the preferred, for the purposes of this invention, is mica due to its commercial availability.

Micas which can be used when practicing this invention include natural micas and synthetic micas. Examples of natural micas include: muscovite ($K_2Al_4(Al_2Si_6O_{20})(OH)_4$), phlogopite ($K_2(Mg,Fe^{2+})_6(Al_2Si_6O_{20})(OH,F)_4$), and biotite
15 ($K_2(Fe^{2+},Mg)_6(Al_2Si_6O_{20})(OH)_4$). Examples of synthetic micas include: fluorophlogopite ($K_2Mg_6Al_2Si_6O_{20}F_4$) and barium disilicic ($Ba_2Mg_6Al_2Si_6O_{20}F_4$). Of the micas which have the aforementioned particle size distribution parameters, the preferred, for the purposes of this invention, is muscovite mica due to its commercial availability.

Gas barrier coatings of this invention can further include other additives
20 known to those skilled in the art. Some of the more common additives which can be present in the gas barrier coating include: pigments, silicones, surfactants, and/or catalysts for coating compositions which involve an epoxy-amine reaction. Each of these specific optional components will be discussed below.

With regard to the use of pigments, in addition to imparting color and/or tint
25 to the gas barrier coating, their use can also further reduce the amount of gas that permeates therethrough. If employed, the weight ratio of pigment to binder is typically not more than about 1:1, preferably not more than about 0.3:1, and more preferably not more than about 0.1:1. The binder weight used in these ratios is the total solids weight of the polyamine-polyepoxide resin in the gas barrier coating.

30 With regard to the use of silicones, they may be included in the gas barrier coating to assist in wetting the thermoplastic, gas-permeable label material over which the barrier coating will be applied. Generally, silicones which can be used for this purpose

- 32 -

include various organosiloxanes such as polydimethylsiloxane, polymethylphenylsiloxane and the like. Specific examples of such include: SF-1023 silicone (a polymethylphenylsiloxane available from General Electric Co.), AF-70 silicone (a polydimethylsiloxane available from General Electric Co.), and DF-100 S silicone (a 5 polydimethylsiloxane available from Mazer Chemicals, a division of PPG Industries, Inc.). If employed, such silicones are typically added to the gas barrier coating in amounts ranging from about 0.01 to about 1.0 percent by weight based on total resin solids in the gas barrier coating.

With regard to the use of surfactants, they are typically included in the 10 aqueous-based versions of the gas barrier coating. Examples of surfactants that can be used for this purpose include any suitable nonionic or anionic surfactant. If employed, such surfactants are typically present in an amount ranging from about 0.01 to about 1.0 percent by weight based on the total weight of the gas barrier coating.

With regard to the use of catalysts, they may be included in the gas barrier 15 coating to aid in the reaction between polyamine (A) and polyepoxide (B). Generally, any suitable catalyst that is used for epoxy-amine reactants can be employed when practicing this invention. Examples of such suitable catalysts include: dihydroxy aromatics (e.g., resorcinol), triphenyl phosphite, calcium nitrate and the like.

Typically, when applying the gas barrier coating onto the labels and/or 20 plastic closures, the components of a gas barrier coating (*i.e.*, polyamine (A) and polyepoxide (B), and filler (C) when present) are first thoroughly mixed together. The mixture can then be immediately applied to the thermoplastic, gas-permeable packaging material, or held for a period of time typically ranging from about 1 minutes to about 60 minutes prior to application to improve cure and/or clarity. This holding time can be reduced and/or 25 eliminated when the initial polyamine is in the form of a polyamine adduct or when the solvent employed is 2-butoxyethanol.

When practicing this invention, the gas barrier coating can be applied onto the labels and/or plastic closures by any conventional means known to those skilled in the art (e.g., spraying, rolling, dipping, brushing and the like). However, for the purposes of this 30 invention, spray, rolling, and/or dipping applications are preferred.

After application of the gas barrier coating, it may be cured at temperatures as low as ambient temperature by allowing for a gradual cure over several hours to several

- 33 -

days. However, such low temperature curing is generally slower than desired for commercial production lines. It is also not an efficient means of removing solvent from the cured barrier coating. Therefore, in one embodiment, the gas barrier coating is cured by being heated at elevated temperatures as high as possible without distorting the thermoplastic, gas-permeable

5 packaging material over which it is applied.

For a relatively "slow" solvent (*i.e.*, a solvent having a relatively low evaporation rate), curing temperatures typically range from about 55° C. to about 110° C., and preferably from about 70° C. to about 95° C. At such curing temperatures, curing times will typically range from about 1 minute to about 60 minutes.

10 For a relatively "fast" solvent (*i.e.*, a solvent having relatively high evaporation rate), curing temperatures typically range from about 35° C. to about 70° C., and preferably from about 45° C. to about 65° C. At such curing temperatures, curing times will typically range from about 0.5 minute to about 30 minutes.

15 As described above, the gas barrier label employed when practicing this invention provides significantly improved gas barrier properties to the resulting plastic packaging container. In addition, this gas barrier label can easily be removed from the plastic packaging container by conventional recycling practices.

EXAMPLES

20 The present invention is more particularly described in the following examples which are intended as illustration only and are not intended to limit the scope thereof. Unless otherwise indicated, all weight percentages are based on the total weight of all the ingredients of the barrier coating being shown in the example.

EXAMPLE 1

This example illustrates the preparation of a polyamine-polyepoxide gas barrier coating for application to the barrier labels of the present invention.

25 A polyamine-polyepoxide gas barrier coating composition was prepared by stirring together the following material: 23.5 weight percent GASKAMINE® 328S (a reaction product of metaxylylenediamine and epichlorohydrin which has been vacuum stripped to remove free MXDA, commercially available from Mitsubishi Gas Company), 72.8 weight percent of DOWANOL® PM (1-methoxy-2-propanol commercially available from Dow

Chemical Company), 0.1 weight percent SF-1023 silicone surfactant from General Electric, 2.4 weight percent of cyclohexyl alcohol (with 2% water), and 1.3 weight percent of deionized water. The resulting homogeneous blend is hereinafter referred to as "Component 1A." All aforementioned weight percentages are based on the total weight of all components in

5 Component 1A.

Then, 75.0 weight percent of DEN-444 (an epoxy novolac resin having a glycidyl functionality of 3.6, commercially available from Dow Chemical Co.), and 25.0 weight percent of methyl ethyl ketone were stirred together. The resulting homogeneous blend is hereinafter referred to as "Component 1B." All aforementioned weight percentages are based
10 on the total weight of all components in Component 1B.

Components 1A and 1B were blended together at a ratio of 3:1 by volume.

The resultant homogeneous blend is hereinafter referred to as "Coating 1".

Multilayer gas barrier labels were prepared by spray applying the gas barrier coating of this example onto one side of polypropylene label stock having an approximate film
15 thickness of 2 mils, the coated side of the polypropylene label having been corona pretreated to facilitate adhesion. The surface area of the label was 16.8 in² (42.6 cm²). Coated labels were cured for 8.5 minutes at 145° F. (63° C.) to yield a dry coating having a thickness ranging from about 0.2 to 0.5 mil. The cured film of the gas barrier coating had a theoretical nitrogen content of about 7.1 weight percent.

20 Coated labels were affixed to uncoated 330 milliliter PET soft drink bottles. The full brim volume capacity of the bottle is 350 ml; and the bottle's surface area is 40 in² (102 cm²). The coated labels were affixed to the uncoated PET containers by wrapping the label around the outer wall of the container and securing the label with tape to simulate the normal commercial practice of using a thin bead of adhesive to secure a label to a container.
25 Coated label (1-A) was affixed with the barrier coating side on the outside with the uncoated thermoplastic polymer layer adjacent the PET bottle surface, the PET bottle having been provided with a 28 millimeter coated closure; coated label (1-B) was affixed with the barrier coating side on the inside, adjacent to the PET bottle surface, the PET bottle having been provided with a 28 millimeter coated closure. An uncoated 330 milliliter PET bottle (1-C)
30 having an uncoated polypropylene label affixed and having been provided with an uncoated 28 millimeter closure was tested in the series as a control.

- 35 -

The top outer surface of polypropylene screw-top bottle closures were coated with about 1 mil of the aforementioned barrier coating, or left uncoated. The barrier coating was cured for about 10 minutes at 145°F. (63°C.). After carbonation treatment of the test bottles, the closures were then screwed onto the test bottles.

5 Bottles with coated and uncoated labels were carbon dioxide treated by filling each bottle with the following mixture: 330 milliliters of water at 40°F. (5°C.); 6.9 g. sodium carbonate (anhydride); and 10.0 g. citric acid dihydrate. Filled containers were quickly capped and gently agitated to mix ingredients. This mixture provided a level of carbonation equivalent to about 4.2 volumes of carbon dioxide. All sealed samples were conditioned by being stored
10 for 2 days at about 70°F. (21°C.) at approximately 50% relative humidity prior to testing.

After the aforementioned conditioning period, samples were tested for carbon dioxide permeability using the Permatran C-IV from Modern Controls, Inc. Results of carbon dioxide permeability testing are provided in the following TABLE 1.

TABLE 1

CONTAINER #	LABEL VARIABLE	CO ₂ PERMEANCE (cc/container/day)
1-A	Coated label	3.6
	Coated face out	
	Coated closure	
1-B	Coated label	2.8
	Coated face (in)	
	Coated closure	
1-C	Uncoated label	3.9
	Uncoated closure	

15

Permeance values in Table 1 are related to GPC (OPC, CPC) as follows:

$$\text{GPC} \times \text{Area} \times \text{Pressure (ATM)} = \text{Permeance}$$

Dry Film Thickness

SUBSTITUTE SHEET (RULE 26)

The results set forth in the above TABLE 1 illustrate the improvement in carbon dioxide permeability of PET soft drink bottles having multilayer gas barrier labels of the present invention affixed to the bottles, i.e., having a typical thermoplastic polymer label coated 5 on one side with a thermosetting gas barrier coating affixed to an uncoated plastic container such that the gas barrier coating is adjacent to the surface of the plastic container.

EXAMPLE 2

This example illustrates the improved carbon dioxide permeability results of 10 PET soft drink bottles demonstrated by the application of the polyamine-polyepoxide gas barrier coating designated in Example 1 as Coating 1, onto the top outer surface of typical polypropylene screw-top plastic bottle closures in conjunction with the multilayer gas barrier label of the present invention.

Multilayer barrier labels were prepared by spray applying the gas barrier 15 coating of Example 1 onto one side of polypropylene label stock having an approximate film thickness of 2 mils, the coated side of the polypropylene label having been corona pretreated to facilitate adhesion. The surface area of the label was 19.7 in² (49.8 cm²). Coated labels were cured for 8.5 minutes at 145° F. (63° C.) to yield a dry coating having a thickness ranging from about 0.2 to 0.5 mil. The cured film of the gas barrier coating had a theoretical nitrogen content 20 of about 7.1 weight percent. Labels so prepared were aged for a period of one week at approximately 70° F. (23°C.) at approximately 50% relative humidity prior to attaching to test bottles.

Coated and uncoated labels were affixed to uncoated twelve ounce (355 milliliters) PET soft drink bottles. The full brim volume of the bottle is 13 ounces (390 ml); 25 and the bottle's surface area is 45 in² (114 cm²). The labels were affixed to the uncoated PET containers by wrapping the label around the outer wall of the container and securing the label with tape to simulate the normal commercial practice of using a thin bead of adhesive to secure a label to a container. Container (2-A) was an uncoated PET bottle with no label and an uncoated closure. Container (2-B) was an uncoated PET bottle with an uncoated label and an 30 uncoated closure. Container (3-A) was an uncoated PET bottle with the multilayer gas barrier label of the present invention, affixed such that the gas barrier coating, Coating 1 of Example 1, was adjacent the PET bottle surface, the PET bottle having been provided with a closure.

- 37 -

The top outer surface of polypropylene screw-top bottle closures were coated with about 1.0 mil of the aforementioned barrier coating, or left uncoated. The barrier coating was cured for about 10 minutes at 145° F. (63° C.). After carbonation treatment of the test bottles, the closures were then screwed onto the test bottles.

5 Bottles with coated and uncoated labels were carbon dioxide treated by filling each bottle with the following mixture: 375 milliliters of water at 40° F. (5°C.); 7.7 g. sodium carbonate; and 11.0 g. citric acid. Filled containers were quickly capped and gently agitated to mix ingredients. This mixture provided a level of carbonation equivalent to about 4.2 volumes of carbon dioxide. All sealed samples were conditioned by being stored for 2 days at about 70°
10 F. (21° C.) at approximately 50% relative humidity prior to testing.

After the aforementioned conditioning period, samples were tested for carbon dioxide permeability using the Permatran C-IV from Modern Controls, Inc. Results of carbon dioxide permeability testing are provided in the following TABLE 2.

15

TABLE 2

CONTAINER #	VARIABLE	CO ₂ PERMEANCE (cc/container/day)
2-A	No label	4.6
	Uncoated closure	
	Uncoated bottle	
2-B	Uncoated label	4.5
	Uncoated closure	
	Uncoated bottle	
2-C	Coated label	2.6
	Coated closure	
	Uncoated bottle	

- 38 -

The results as set forth in the above TABLE 2 illustrate the improved carbon dioxide permeability demonstrated by the use of the multilayer gas barrier label of the present invention in conjunction with the use of typical polyolefin bottle closures which have been coated on the top outer surface with the thermosetting polyamine-polyepoxide gas barrier

5 coating of Example 1.

It is evident from the foregoing that various modifications, which are apparent to those skilled in the art, can be made to the embodiments of this invention without departing

10 from the spirit or scope thereof. Having thus described the invention, it is claimed as follows.

What Is Claimed Is:

1. A sealable plastic packaging container designed to store items that are carbonated, oxygen-sensitive, or both, said container comprising:
 - 5 (a) a plastic package body having an interior surface which defines a cavity and an exterior surface having an opening defined therein through which an oxygen-sensitive and/or carbonated item can be introduced into the cavity defined by the package body's interior surface,
 - (b) a closure configured to seal the opening defined through the package body's exterior surface, and
 - 10 (c) a gas barrier label configured to cover at least 30% of the package body's exterior surface, said gas barrier label comprising:
 - (i) a layer of a thermoplastic, gas-permeable label material; and
 - (ii) a layer of a thermosetting gas barrier material coated onto at least one surface of the thermoplastic, gas-permeable label material layer, wherein said gas barrier layer label is affixed to said package body's exterior surface such that the thermosetting gas barrier material layer is in intimate contact therewith.
- 20 2. The plastic packaging container of claim 1 wherein the gas barrier coating material comprises the reaction product of a polyamine (A) and polyepoxide (B), wherein polyamine (A) comprises at least one of the following:
 - (a) an initial polyamine;
 - (b) an ungelled amine-epoxide adduct having active amine hydrogens which is the reaction product of the initial polyamine and at least one of the following:
 - (i) epichlorohydrin, and
 - (ii) a polyepoxide having a plurality of glycidyl groups linked to an aromatic member; or
 - 25 (c) initial polyamine reacted with formaldehyde and a phenol
- 30 $\mathbf{R}^5\text{-OH}$
where \mathbf{R}^5 is an aromatic group or fused aromatic group which may contain alkyl substitutions of 1-4 carbon atoms.

- 40 -

3. The plastic packaging container of claim 1 wherein label graphics are interposed between the thermoplastic, gas-permeable label material layer and the gas barrier material layer.

5

4. The plastic packaging container of claim 1 wherein label graphics are reverse printed onto the gas barrier material layer such that said label graphics are interposed between the gas barrier material layer and the package body's exterior surface.

10

5. The plastic packaging container of claim 1 wherein the thermoplastic, gas-permeable label material comprises: a polyolefin, a polyamide, a polyester or any mixture thereof.

15 6. The plastic packaging container of claim 2 wherein at least 50 percent of the carbon atoms in the initial polyamine are in one or more aromatic rings.

7. The plastic packaging container of claim 2 wherein the initial polyamine is represented by the structure:

20



where:

k is 1.5 or greater,

Φ is an aromatic-containing compound, and

R^1 is an alkyl group having from 1 to 4 carbon atoms.

25

8. The plastic packaging container of claim 7 wherein k is 1.9 or greater and R^1 is an alkyl group which does not have more than 2 carbon atoms.

30

9. The plastic packaging container of claim 2 wherein from about 10 to about 80 percent of the ungelled amine-epoxide adduct's active amine hydrogens are reacted with epoxy groups prior to reacting the ungelled amine-epoxide adduct with polyepoxide (B).

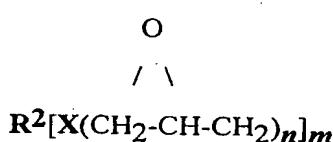
- 41 -

10. The plastic packaging container of claim 2 wherein polyamine (A) comprises an ungelled amine-epoxide adduct which is the reaction product of the initial polyamine and epichlorohydrin.

5 11. The plastic packaging container of claim 2 wherein the initial polyamine comprises m-xylylenediamine.

10 12. The plastic packaging container of claim 2 wherein polyamine (A) comprises an ungelled amine-epoxide adduct which is the reaction product of the initial polyamine and a polyepoxide having a plurality of glycidyl groups linked to an aromatic member.

15 13. The plastic packaging container of claim 2 wherein the polyepoxide having a plurality of glycidyl groups linked to an aromatic member is represented by the structure:



where:

20 R^2 is phenylene or naphthylene;

X is N, NR^3 , CH_2N , CH_2NR^3 , O, and/or $\text{C}(\text{O})-\text{O}$, where R^3 is an alkyl group containing from 1 to 4 carbon atoms, a cyanoethyl group or cyanopropyl group;

n is a number 1 or 2; and

25 m is a number from 2 to 4.

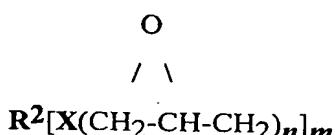
14. The plastic packaging container of claim 13 wherein the polyepoxide having a plurality of glycidyl groups linked to an aromatic member comprises at least one of the following: N,N,N',N'-tetrakis (oxiranylmethyl)-1,3-benzene dimethanamine, resorcinol 30 diglycidyl ether, diglycidyl esters of phthalic acid and triglycidyl para-aminophenol.

- 42 -

15. The plastic packaging container of claim 2 wherein polyepoxide (B) comprises a polyepoxide having a plurality of glycidyl groups linked to an aromatic member.

16. The plastic packaging container of claim 15 wherein polyamine (A) comprises
5 m-xylylenediamine.

17. The plastic container of claim 15 wherein the polyepoxide having a plurality of glycidyl groups linked to an aromatic member is represented by the structure:



where:

R² is phenylene or naphthylene:

X is N, NR³, CH₂N, CH₂NR³, O, and/or C(O)-O, where R³ is an alkyl group containing from 1 to 4 carbon atoms, a cyanoethyl group or cyanopropyl group;

n is a number 1 or 2; and

m is a number from 2 to 4

20 18. The plastic packaging container of claim 17 wherein the polyepoxide having a plurality of glycidyl groups linked to an aromatic member comprises at least one of the following: N,N,N',N'-tetrakis (oxiranylmethyl)-1,3-benzene dimethanamine, resorcinol diglycidyl ether, diglycidyl esters of phthalic acid and triglycidyl para-aminophenol.

25 19. The plastic packaging container of claim 2 wherein the reaction product of polyamine (A) and polyepoxide (B) comprises filler (C) which comprises a platelet-type filler with the following particle size distribution:

- (a) a number mean particle diameter in the range from about 5.5 to about 15 microns, and
- (b) a volume mean particle diameter in the range from about 8 to about 25 microns.

- 43 -

20. A sealable plastic packaging container designed to store items that are carbonated, oxygen-sensitive, or both, said container comprising:

- (a) a plastic package body having an interior surface which defines a cavity and an exterior surface having an opening defined therein through which an oxygen-sensitive and/or carbonated item can be introduced into the cavity defined by the package body's interior surface,
- (b) a label configured to cover at least 30% of the package body's exterior surface said layer label being affixed to said package body's exterior surface,
- (c) a gas barrier closure configured to seal the opening defined through the package body's exterior surface, said gas barrier closure comprising:
 - (i) a thermoplastic, gas-permeable closure body; and
 - (ii) a layer of a thermosetting gas barrier material coated onto at least one surface of the thermoplastic, gas-permeable closure body.

15 21. The plastic packaging container of claim 20 wherein said label is a gas-permeable label that comprises:

- (a) a layer of a thermoplastic, gas-permeable label material; and
- (b) a layer of a thermosetting gas barrier material coated onto at least one surface of the thermoplastic, gas-permeable label material layer, and

20 wherein said gas barrier layer label is affixed to said package body's exterior surface such that the thermosetting gas barrier material layer is in intimate contact therewith.

25 22. The plastic packaging container of claim 21 wherein the gas barrier coating material on the gas barrier closure comprises the reaction product of a polyamine (A) and polyepoxide (B), wherein polyamine (A) comprises at least one of the following:

- (a) an initial polyamine;
- (b) an ungelled amine-epoxide adduct having active amine hydrogens which is the reaction product of the initial polyamine and at least one of the following:
 - (i) epichlorohydrin, and
 - (ii) a polyepoxide having a plurality of glycidyl groups linked to an aromatic member; or

- 44 -

(c) initial polyamine reacted with formaldehyde and a phenol

R^5-OH

where R^5 is an aromatic group or fused aromatic group which may contain alkyl substitutions of 1-4 carbon atoms.

5

23. The plastic packaging container of claim 21 wherein the gas barrier coating material on the gas barrier label comprises the reaction product of a polyamine (A) and polyepoxide (B), wherein polyamine (A) comprises at least one of the following:

(a) an initial polyamine;

10 (b) an ungelled amine-epoxide adduct having active amine hydrogens which is the reaction product of the initial polyamine and at least one of the following:

(i) epichlorohydrin, and

(ii) a polyepoxide having a plurality of glycidyl groups linked to an aromatic member; or

15 (c) initial polyamine reacted with formaldehyde and a phenol

R^5-OH

where R^5 is an aromatic group or fused aromatic group which may contain alkyl substitutions of 1-4 carbon atoms.

20

24. The plastic packaging container of claim 23 wherein the gas barrier coating material on the gas barrier closure comprises the reaction product of a polyamine (A) and polyepoxide (B), wherein polyamine (A) comprises at least one of the following:

(a) an initial polyamine;

25 (b) an ungelled amine-epoxide adduct having active amine hydrogens which is the reaction product of the initial polyamine and at least one of the following:

(i) epichlorohydrin, and

(ii) a polyepoxide having a plurality of glycidyl groups linked to an aromatic member; or

(c) initial polyamine reacted with formaldehyde and a phenol

R^5-OH

30 where R^5 is an aromatic group or fused aromatic group which may contain alkyl substitutions of 1-4 carbon atoms.

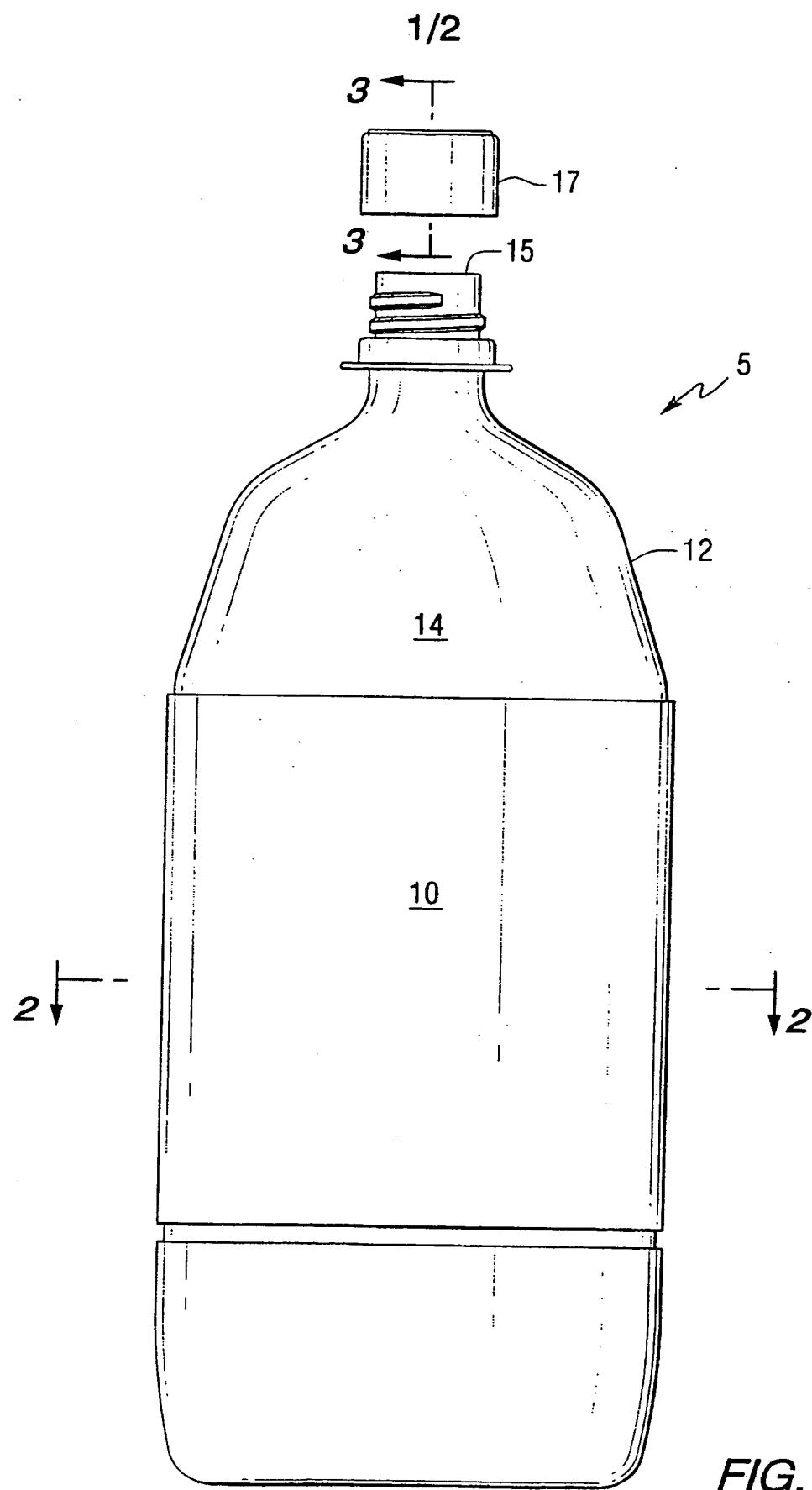


FIG. 1

2/2

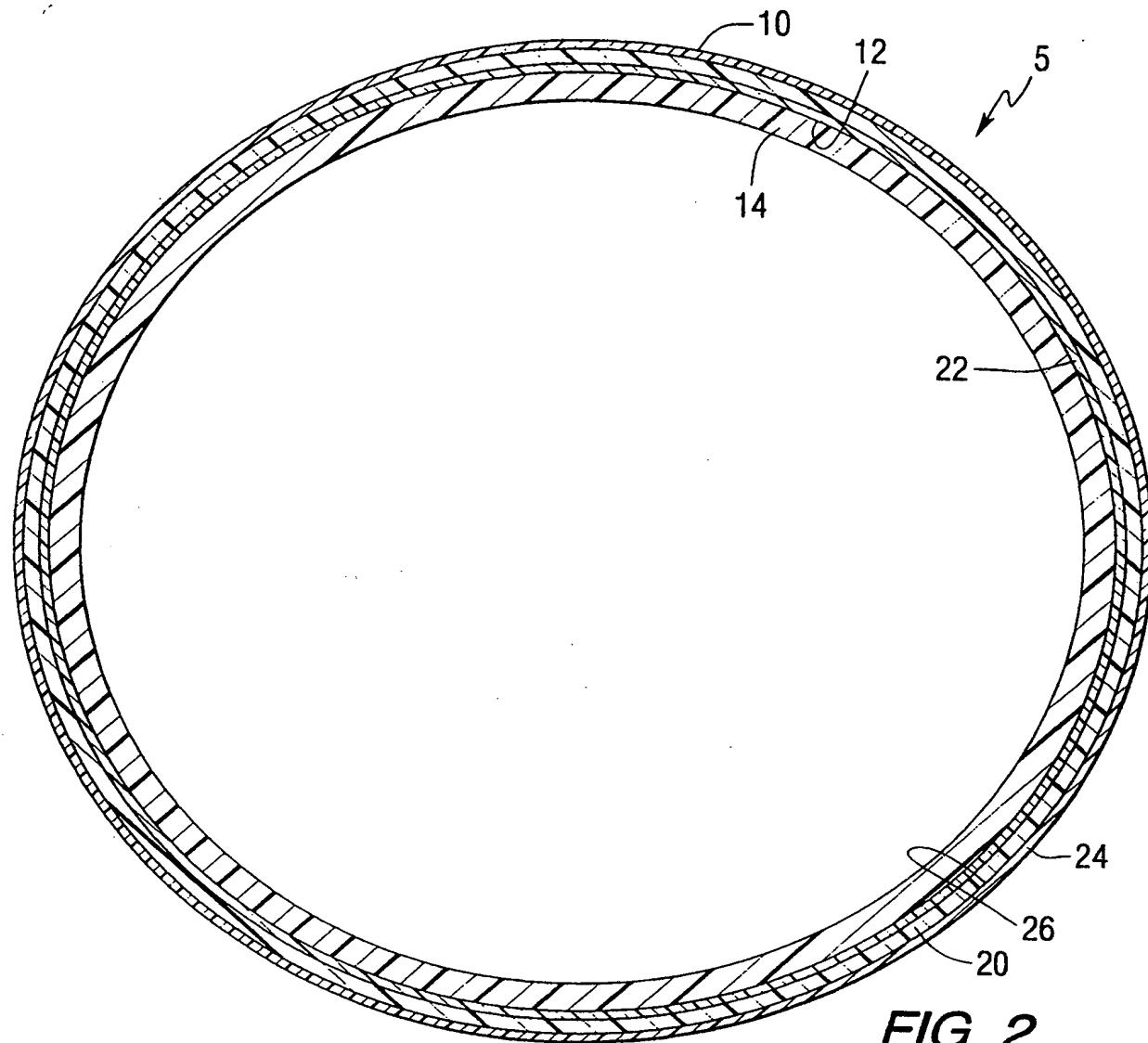


FIG. 2

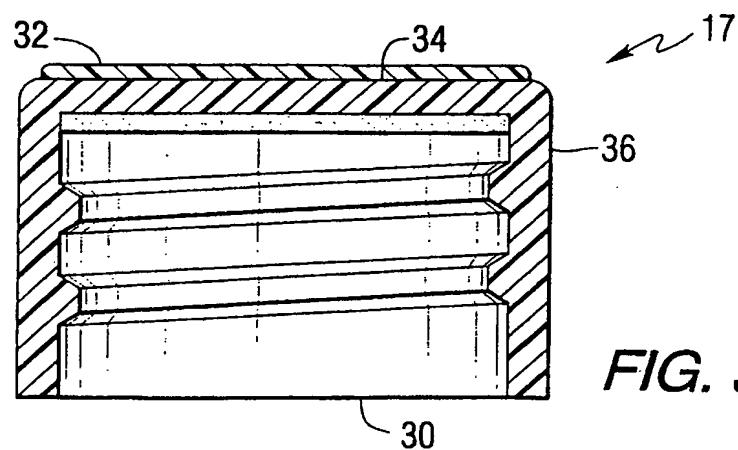


FIG. 3

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

Inte...inal Application No

PCT/US 98/16839

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B65D23/08 C08G59/18

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B65D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 26997 A (PPG INDUSTRIES INC) 12 October 1995 cited in the application see page 4, line 9 - page 5, line 2 see page 10, line 23 - page 11, line 12 see page 13, line 22 - page 14, line 8 see page 18, line 8 - line 13 see page 21, line 4 - line 9 ---	1-19
Y	GB 2 310 187 A (KAO CORP) 20 August 1997 see abstract ---	20-24
Y	GB 2 205 295 A (HART REGINALD JAMES) 7 December 1988 see page 2, line 34 - page 3, line 3 ---	20-24
A	GB 2 205 295 A (HART REGINALD JAMES) 7 December 1988 see page 2, line 34 - page 3, line 3 ---	1 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 November 1998

Date of mailing of the international search report

03/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Attalla, G

INTERNATIONAL SEARCH REPORT

Int. Jnl Application No
PCT/US 98/16839

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 232 754 A (WAUGH RICHARD A) 3 August 1993 see column 2, line 16 - line 18 -----	2
A	US 4 658 974 A (FUJITA TAKASHI ET AL) 21 April 1987 see column 3, line 12 - line 21 -----	3,4
A	EP 0 327 039 A (PPG INDUSTRIES INC) 9 August 1989 see abstract -----	2
A	EP 0 327 038 A (PPG INDUSTRIES INC) 9 August 1989 see abstract -----	2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/16839

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
WO 9526997	A 12-10-1995	AU	685918 B		29-01-1998
		AU	1839495 A		23-10-1995
		BG	100880 A		31-07-1997
		BR	9507448 A		12-08-1997
		CA	2184406 A		12-10-1995
		CZ	9602827 A		12-03-1997
		EP	0754200 A		22-01-1997
		FI	963895 A		27-09-1996
		HU	75189 A		28-04-1997
		JP	9511537 T		18-11-1997
		NO	964105 A		13-11-1996
		NZ	281449 A		27-07-1997
		PL	316620 A		20-01-1997
		SK	122296 A		10-09-1997
GB 2310187	A 20-08-1997	JP	9221179 A		26-08-1997
		DE	19704665 A		06-11-1997
		US	5791465 A		11-08-1998
GB 2205295	A 07-12-1988	NONE			
US 5232754	A 03-08-1993	NONE			
US 4658974	A 21-04-1987	NONE			
EP 0327039	A 09-08-1989	CA	1337137 A		26-09-1995
		DE	68928668 D		18-06-1998
		DE	68928668 T		26-11-1998
		ES	2116261 T		16-07-1998
		JP	2004820 A		09-01-1990
		JP	2057215 C		23-05-1996
		JP	7091368 B		04-10-1995
		MX	166278 B		28-12-1992
		MX	9205371 A		31-03-1994
		US	5489455 A		06-02-1996
		US	5438109 A		01-08-1995
		US	5008137 A		16-04-1991
		US	5491204 A		13-02-1996
		US	5573819 A		12-11-1996
		US	5300541 A		05-04-1994
EP 0327038	A 09-08-1989	CA	1337229 A		03-10-1995
		DE	68922416 D		08-06-1995
		DE	68922416 T		01-02-1996
		ES	2074447 T		16-09-1995
		JP	1240515 A		26-09-1989
		JP	2057214 C		23-05-1996
		JP	7091367 B		04-10-1995
		US	5006381 A		09-04-1991
		US	5639848 A		17-06-1997